

Polarizability of molecular chains: does one need exact exchange?

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Standard density functional approximations greatly over-estimate the static polarizability of long-chain polymers, but Hartree-Fock or exact exchange calculations do not. Simple self-interaction corrected (SIC) approximations can be even better than exact exchange, while their computational cost can scale only linearly with the number of occupied orbitals.

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Ground-state Kohn-Sham (KS) density functional theory (DFT) has become extraordinarily popular for solving electronic structure problems in solid-state physics, quantum chemistry and materials science [1]. The accuracy of modern generalized gradient approximations (GGAs) and hybrid functionals has proven sufficient for many applications, often with surprisingly small errors. Bond dissociation energies, geometries, phonons, etc., are now routinely calculated with errors of 10-20%.

But local and gradient-corrected functionals overestimate massively the static polarizability and hyperpolarizability of molecular chains, especially conjugated polymers. This failure has been the subject of many studies over the last decade [2, 3, 4, 5, 6, 7, 8, 9, 10], studies which highlight the important role played by the response field originating from the exchange-correlation (XC) potential. The exact induced XC field counteracts the applied external field, keeping the polarization low. In the local (or gradient-corrected) density approximation (LDA), this field erroneously points in the *same* direction as the applied field [3, 4, 5]. Such failures of standard functionals appear in other contexts, such as transport through single molecules [11], or the polarizability of large molecules.

In contrast, these effects are easily captured within standard wavefunction theory. In particular, Hartree-Fock (HF) theory does not greatly overestimate the polarizabilities and provides a good starting point for more accurate wavefunction treatments, such as Möller-Plesset (MP) perturbation theory. Thus exact exchange (EXX) DFT, the KS-DFT method for minimizing the HF energy while retaining a single multiplicative potential, provides a promising alternative and indeed has been found to give results very similar to HF [4, 8, 10]. This improvement can be attributed to the orbital-dependence of EXX, and the lack of self-interaction error [8], i.e. EXX is exact for one electron, unlike LDA or GGA.

However, EXX is only one among many possible self-interaction free functionals that one may construct. In fact any GGA can be corrected to become self-interaction free (self-interaction corrected - SIC) by direct subtraction of the XC functional evaluated on each of the individual orbitals [12]. While this can be performed for either LDA or GGA, only LDA has significantly improved energetics from this procedure, but many investigators

are searching for useful methods to correct GGA's for self-interaction [13]. More importantly, EXX includes a sum over all *unoccupied* orbitals, while SIC functionals use only occupied ones, i.e., EXX can often be substantially more expensive computationally. So the question then becomes: does one really need EXX, or will any self-interaction free functional perform equally well?

We perform SIC calculations for the polarizabilities of hydrogenic chains using LDA and GGA. Our SIC potential is constructed using the optimized effective potential (OEP) framework within the Krieger-Li-Iafrate (KLI) approximation [14]. Using results from accurate wave-function methods as a benchmark, we find that the polarizabilities calculated with KLI-SIC are in better agreement than those obtained with KLI exact exchange (X-KLI), with the remaining error attributed to the KLI approximation [10, 15]. This is an important result since KLI-SIC scales only linearly with the number of occupied Kohn-Sham (KS) orbitals, as compared with the quadratic scaling of X-KLI. Thus SIC becomes a valuable scheme for evaluating the static polarizability of polymers with large unit cells, and in other applications where these effects may be important [11].

We start with a brief description of the SIC method used in this work. In DFT [16], the total energy functional $E[\rho^\uparrow, \rho^\downarrow]$ (ρ^σ is the spin $\sigma = \uparrow, \downarrow$ density, $\rho = \sum_\sigma \rho^\sigma$) can be written as

$$E[\rho^\uparrow, \rho^\downarrow] = T_S[\rho] + \int d^3\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}) + U[\rho] + E_{xc}[\rho^\uparrow, \rho^\downarrow], \quad (1)$$

with T_S the kinetic energy of the non-interacting KS orbitals, $v(\mathbf{r})$ the external potential, U the Hartree energy, and E_{xc} the XC energy. For any GGA

$$E_{xc}^{SIC}[\{\rho_n^\sigma\}] = E_{xc}^{GGA}[\rho^\uparrow, \rho^\downarrow] - \sum_{n\sigma}^{\text{occupied}} (U[\rho_n^\sigma] + E_{xc}^{GGA}[\rho_n^\sigma, 0]), \quad (2)$$

where $\rho_n^\sigma = |\psi_n^\sigma|^2$ is the density of the n -th KS orbital. Levy's minimization [17] leads to a set of single particle KS-like equations for ψ_n^σ with corresponding eigenvalues $\epsilon_n^{\sigma, SIC}$ and occupation numbers p_n^σ ($\rho^\sigma = \sum_n p_n^\sigma \rho_n^\sigma$)

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{eff},n}(\mathbf{r}) \right] \psi_n^\sigma = \epsilon_n^{\sigma, SIC} \psi_n^\sigma. \quad (3)$$

The effective potential $v_{\text{eff},n}^\sigma(\mathbf{r})$ is now KS-orbital dependent and cannot be classified as a standard multiplicative KS-potential. For instance it is ambiguously defined for unoccupied KS-orbitals since the SIC is only defined for the occupied ones. The solution of equation (3) has followed several approaches. The simplest one is to solve it directly under a normalization constraint with the resulting non-orthogonal orbitals undergoing an orthogonalization procedure [12]. This scheme however is not free of complications, since $E_{\text{xc}}^{\text{SIC}}$ is not invariant under a unitary transformations of the occupied $\{\psi_n^\sigma\}$. The solution [18] is then to work with an auxiliary set of localized orbitals $\{\phi_n^\sigma\}$ used for constructing $v_{\text{eff},n}^\sigma(\mathbf{r})$ and related to $\{\psi_n^\sigma\}$ by a unitary transformation chosen so as to minimize $E_{\text{xc}}^{\text{SIC}}$.

A convenient alternative is offered by the OEP method [19] where the orbital-dependent $v_{\text{eff},n}^\sigma(\mathbf{r})$ is recast into a local multiplicative orbital-independent potential. In this way the SIC problem can then be solved as a normal KS problem. However the construction of an OEP is computationally demanding. Here we adopt the KLI approximation [14], which is practically easy to construct and retains most of the advantages of the full OEP, being therefore well suited to the SIC problem [20]. The orbital-independent KLI effective SIC Kohn-Sham potential takes the form

$$v_{\text{KS}}^\sigma(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}^{\sigma,\text{GGA}}(\mathbf{r}) + v_{\text{xc}}^{\sigma,\text{SIC}}(\mathbf{r}), \quad (4)$$

where v_{H} and $v_{\text{xc}}^{\sigma,\text{GGA}}$ are the Hartree and GGA-XC potentials. We define the SIC potentials by

$$u_n^{\sigma,\text{SIC}}(\mathbf{r}) = -v_{\text{Hxc}}^{\sigma,\text{GGA}}[\tilde{\rho}_n^\sigma, 0](\mathbf{r}), \quad (5)$$

where v_{Hxc} is the sum of the Hartree and GGA potentials, and their Slater average as

$$w_{\text{xc}}^{\sigma,\text{SIC}}(\mathbf{r}) = \sum_{n=1}^{N^\sigma} \tilde{f}_n^\sigma(\mathbf{r}) u_n^{\sigma,\text{SIC}}(\mathbf{r}), \quad (6)$$

where $\tilde{f}_n^\sigma(\mathbf{r}) = \tilde{\rho}_n^\sigma(\mathbf{r})/\rho^\sigma(\mathbf{r})$ is the auxiliary orbital density as a fraction of the spin-density of its spin. Then

$$v_{\text{xc}}^{\sigma,\text{SIC}}(\mathbf{r}) = w_{\text{xc}}^{\sigma,\text{SIC}}(\mathbf{r}) + \sum_{n=1}^{N^\sigma} \tilde{f}_n^\sigma(\mathbf{r}) [\Delta v_n^{\sigma,\text{SIC}} - C^\sigma]. \quad (7)$$

The orbital densities $\tilde{\rho}_n^\sigma$ in Eqs. (5)-(7) are calculated from the auxiliary set of localized orbitals $\{\phi_i^\sigma\}$ instead of the canonical $\{\psi_i^\sigma\}$. Both sets of orbitals give the same total density ρ^σ . The orbital shift terms $\Delta v_n^{\sigma,\text{SIC}}$ (being a constant), are obtained by solving

$$\sum_{n=1}^{N^\sigma} (\delta_{nm} - \tilde{f}_{nm}^\sigma) \Delta v_n^{\sigma,\text{SIC}} = \bar{w}_{\text{xc},m}^{\sigma,\text{SIC}} - \bar{u}_m^{\sigma,\text{SIC}}, \quad (8)$$

where $\bar{h}_m^\sigma = \int d\mathbf{r} \tilde{\rho}_m^\sigma(\mathbf{r}) h^\sigma(\mathbf{r})$. Furthermore,

$$\sum_{n=1}^{N^\sigma} \tilde{f}_{nm}^\sigma = 1, \quad \sum_{n=1}^{N^\sigma} (\bar{w}_{\text{xc},m}^{\sigma,\text{SIC}} - \bar{u}_m^{\sigma,\text{SIC}}) = 0, \quad (9)$$

so that the linear system in Eq.(8) is of rank $(N^\sigma-1)$ and must be solved using a least squares approach. The constant C^σ is set to $\Delta v_{\text{HOMO}}^{\sigma,\text{SIC}}$ (HOMO is the highest occupied molecular orbital). We have implemented this scheme in the DFT code SIESTA [21].

To facilitate easy comparison with previous quantum chemistry and EXX-DFT calculations [10], we chose as a test system the widely studied linear hydrogen chains H_n made up of n H atoms with alternating H-H distances of 2 and 3 a_0 . An optimized atomic orbital basis set consisting of double zeta polarized s and triple zeta polarized p functions is employed. The Pipek-Mezey localization

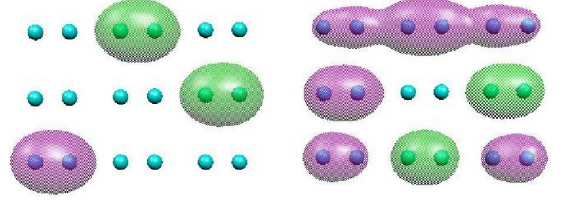


FIG. 1: The Pipek-Mezey localized molecular orbitals $\{\phi_i^\sigma\}$ (left) and canonical Kohn-Sham orbitals $\{\psi_i^\sigma\}$ (right) for the occupied states of the H_6 molecule.

scheme [22] which minimizes the number of atoms over which a given molecular orbital is delocalized, is used to transform the canonical KS-orbitals $\{\psi_n^\sigma\}$ into the localized set $\{\phi_n^\sigma\}$. As an example both the $\{\phi_n^\sigma\}$ and the $\{\psi_n^\sigma\}$ of H_6 are presented in figure 1. Finally the static polarizability $\alpha = \delta\mu_z/\delta F_z$ is calculated numerically using finite differences.

Table I contains the central results of this work. The first column contains highly accurate (MP4) quantum chemical results, which we take as exact. The next two columns show LDA and PBE results [23], demonstrating the LDA overestimate (by about 100% for H_{12}) of α , an overestimate that is only slightly reduced by GGA. We checked several GGA's, and they all had the same features. Small finite systems, such as atoms, are well-known to overpolarize in LDA and GGA, because their XC potentials are too shallow, and do not decay with the correct asymptotic form, $-1/r$. But this is a distinct effect from that discussed here, which is due to the response to the electric field inside the molecule. Ours is a bulk effect, not depending on the end points. We checked this and found that the LB94 functional [24], specifically designed to reproduce the correct asymptotic behavior, does not yield any better results than the other GGA's and in fact worsens the LDA α .

The next 3 columns list results of different types of calculations using the Fock integral, and no correlation. We note that HF slightly overestimates the polarizability, but by less than 10%. An exact OEP treatment of the same functional (X-OEP) yields essentially the same numbers. Our KLI scheme, applied to the same functional (X-KLI), makes a noticeable overestimate, but the error remains less than 20%, compared to OEP.

Now we focus on the SIC results. Regardless of the

TABLE I: Calculated polarizability α of H_n chains obtained by using the KLI-SIC method with different XC functionals. The subscript X indicates that correlation has been dropped from the XC potential. These are compared with MP4, HF and exact exchange DFT (EXX) results from reference [10].

H_N	exact	GGA		EXX			KLI-SIC			X-only			
	MP4	LDA	PBE	HF	X-OEP	X-KLI	LDA	PBE	LDA-OEP ^a [15]	LDA _X	PBE _X	SIC-LDA _X	SIC-PBE _X
H ₄	29.5	37.26	35.62	32.0	32.2	33.11	33.38	33.14	32.5	38.90	36.51	33.37	33.10
H ₆	51.6	73.10	69.35	56.4	56.6	60.64	58.56	58.07	54.6	76.16	70.45	58.84	57.63
H ₈	75.9	116.58	109.74	82.3	84.2	91.56	86.94	86.48	76.4	121.64	110.84	87.08	84.53
H ₁₀	—	166.36	155.31	—	—	124.87	117.28	116.16	—	173.89	156.45	116.77	113.14
H ₁₂	126.9	220.55	204.53	137.6	138.1	159.27	147.96	145.98	126.8	231.25	205.51	147.19	141.90

^aEstimated by subtracting the difference between X-KLI and X-OEP.

GGA functional used, the KLI-SIC polarizabilities show a drastic improvement with respect to those obtained with pure GGA. Furthermore, PBE results are very close to LDA results. There remains about a 20% overestimate for H₁₂, but this is probably due to the KLI approximation. Correcting the KLI-SIC-LDA values, using the difference between KLI and OEP for EXX as an error estimate, suggests that OEP-SIC results (*Cf.* Korzdorfer *et al.*[15]) might be in good agreement with MP4. These corrected values are listed under LDA-OEP in Table I.

We also checked if the inclusion of correlation was important for the excellent KLI-SIC results, by running the calculations with correlation removed. For the pure functionals, LDA correlation slightly reduces the huge overestimate, whereas PBE correlation has almost no effect. On the other hand, for the KLI-SIC results, LDA correlation has almost no effect, while PBE correlation corrects the PBE_X result in the *wrong* direction. This is consistent with the general result that SIC-GGA includes some incorrect overcounting of gradient effects [13].

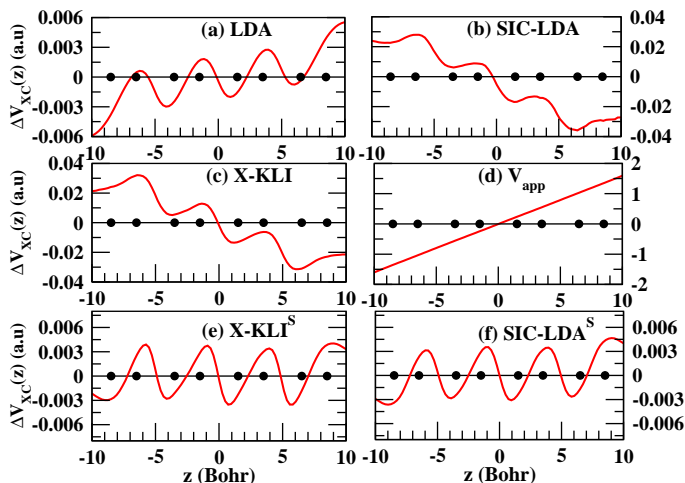


FIG. 2: $\Delta V_{XC}(z) = V_{XC}^E(z) - V_{XC}$ for H_8 plotted against position (z) for (a) LDA, (b) SIC-LDA, (c) X-KLI, (e) X-KLI^S and (f) SIC-LDA^S. The applied external field is shown in (d) and the black dots indicate the position of the H atoms.

The improved response obtained with orbital de-

TABLE II: Static polarizability α of H_n obtained from SIC and X-KLI where only the Slater term in the KLI potential is used (super-script S). Both XC and X-only results are shown for the SIC-LDA^S and SIC-PBE^S.

H_N	SIC-LDA ^S	SIC-PBE ^S	SIC-LDA _X ^S	SIC-PBE _X ^S	X-KLI ^S
H ₄	35.37	35.12	36.25	35.16	35.78
H ₆	67.74	67.13	68.92	66.34	69.17
H ₈	105.91	104.89	107.57	102.97	108.72
H ₁₀	148.64	146.18	150.86	143.10	152.90
H ₁₂	193.94	190.47	197.05	185.25	199.91

pendent functionals is due the opposing XC field, already demonstrated in the literature for OEP exact exchange[10]. Here we verify that the same happens with the KLI-SIC scheme. In figure 2 we plot ΔV_{XC} defined as the difference between the XC potential with and without an applied electric field $\Delta V_{XC}(z) = V_{XC}^E(z) - V_{XC}$ for LDA, SIC-LDA and X-KLI. We denote by a superscript S results obtained by including only the Slater average potential in Eq. (7), dropping the constant terms. Clearly both contributions are significant in the final XC potential. The Slater-only polarizabilities are shown in table II and reflect this.

By comparing the values of α in the tables I and II one may conclude that the Slater average already contains important corrections, but the bulk of the effect is contained in the orbital shift term. For example if one considers the α calculated with LDA for H₁₂ the polarizability is 220.5 for LDA, 193.9 for SIC-LDA^S and 147.9 for SIC-LDA. It is also interesting to note that even at the level of the Slater average, SIC performs better than X-KLI. This can be understood by looking at the XC potential for SIC-PBE^S and X-KLI^S (Fig. 3) when no external field is applied. The SIC-PBE potential exhibits higher peaks in the inter-molecular space between H₂ units than X-KLI. This explains the quantitative difference in α between the two cases. The improved performance of X-OEP over X-KLI can be attributed [10] to similar barriers in the inter-molecular region which however arise from the response part of the X-OEP potential.

Finally we ask whether similar results can be obtained with atomic-like corrections, which have the effect of

making the KS potential deeper at the atomic sites. We investigated both the LDA+U [25] and the atomic LDA-SIC (ASIC) methods [26, 27] in this regard. The LDA+U results are extremely poor, as it provides polarizabilities larger than even those obtained with simple LDA. The ASIC results are far more promising, being half-way between those of GGA and of SIC ($\alpha=33.95, 63.67, 98.39, 137.42, 178.87$ for H_n respectively with $n=4, 6, 8, 10, 12$). In fact, if the ASIC corrections relative to pure LDA were double those we found, they would reproduce the HF results very accurately.

The above can be understood by the way the atomic corrections are introduced. The H atoms are half-filled in the absence of an external field. Switching on the field produces a tiny charge transfer, which however is amplified by the LDA+U potential. As a result the already wrong LDA response field gets amplified. The same does not happen with ASIC, which improves the response over LDA by virtue of the higher inter-molecular barriers.

In conclusion we have demonstrated that SIC functionals at the KLI level, in general, perform better than X-KLI at computing the static polarizability of hydrogenic chains. This is an interesting result in view of the considerably less computational overheads involved with

the SIC method with respect to EXX. Our work therefore opens the prospect of using SIC for evaluating the electrical response of complex polymeric materials.

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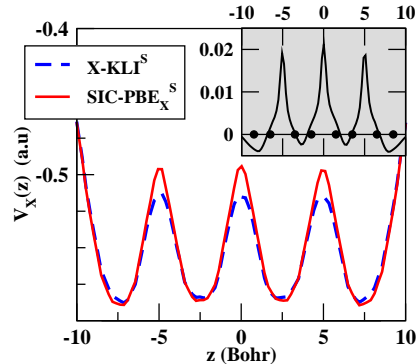


FIG. 3: XC potential plotted against distance (z) for SIC-PBE^S (solid line) and X-KLI^S. The grey inset plots the difference between the two potentials.

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